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ORIGINAL ARTICLE

Microwave-assisted batch and continuous transesterification of karanja oil: process variables optimization and effectiveness of irradiation

Microwave-assisted transesterification of karanja oil

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Abstract The technological advancement in biodiesel production has been the focus area for last the few years and microwave-assisted biodiesel synthesis is one such promising new technology. In the present investigation, microwave irradiation was used to produce biodiesel from non-edible Karanja (*Pongamia pinnata*) oil in batch and continuous mode. Experiments were conducted to understand the effect of volume of the reaction mixture, irradiation time, and irradiation power on the yield of biodiesel. To increase the effectiveness of the microwave irradiation, biodiesel was synthesized in a continuous tubular reactor at two different holdup volumes. The effect of process parameters viz., irradiation time, irradiation power, and methanol to oil ratio were optimized using Box–Behnken experimental design. The effectiveness of microwave irradiation for the different process conditions have been represented through an effectiveness factor. The results reinforce the advantages of continuous processes over batch processes for the production of biodiesel. The properties of biodiesel, namely ester content, density, viscosity, acid value, and cetane index were analyzed and found to be within the limits as prescribed in ASTM D6751-09 standards. The experimental results that have been obtained in this study would be very useful in the scale-up of the microwave-assisted biodiesel process.

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1 Introduction

Biodiesel is a mixture of mono alkyl esters of long-chain fatty acids, an alternative fuel that resembles the diesel fuel. It is derived from triglycerides found in the oils, animal fats, or used cooking oils. Major feed stocks used for the production of biodiesel include the edible oils like rapeseed [1], sunflower [2], palm oil [3], and soybean [4]. To make the production inexpensive and for better food security, low-cost oils like waste cooking oils [5], non-edible oils like *Jatropha* [6], *Pongamia pinnata* [7], and rubber seed oil [8] have been intensively investigated as potential biodiesel sources. In India, Karanja (*P. pinnata*, family—Leguminaceae) is a forest-based under utilized non-edible oil-seed-bearing tree, with an annual production potential of 135,000 million tonnes [9] makes it a good feed stock for the biodiesel production. The government of Karnataka under its biodiesel policy is promoting production of biodiesel from karanja oil. Karanja tree requires no care and can be grown in the waste lands. It is a medium-sized tree that attains a height of about 18 m and a trunk diameter greater than 50 cm. The fresh extracted oil is yellowish orange to brown in color [9]. Meher et al. [7] extracted oil from karanja seeds and produced biodiesel using potassium hydroxide in a conventional mode of heating. The acid value of 5.06 mg KOH/g oil (free fatty acid = 2.5 %) content was reduced to 0.6 mg KOH/g oil (free fatty acid = 0.3 %) by neutralizing with KOH. The neutralization was necessary in order to increase the biodiesel yield.

Biodiesel is generally synthesized in conventional mode [7], both in batch and continuous process. There are several

problems involving transfer of mass between different phases, reaction equilibrium, and costs associated with the conventional mode. In order to avoid these problems different technologies have been developed for the synthesis of biodiesel which includes lipase catalyzed method [10], use of subcritical methanol [1] or supercritical ethanol [11], ultrasonic method [12], static mixers as reactors[13], micro channel reactors [14], oscillatory flow reactors [15], cavitational reactors [16], rotating/spinning tube reactors [17], membrane reactors [18], reactive distillation [19], centrifugal contactors [20], and application of microwave irradiation [4, 21, 22]. Application of microwave irradiation for biodiesel synthesis is more efficient in reducing the time required for the reaction and separation of the products and offers a better way to synthesize biodiesel when compared to conventional mode of heating [23–26].

Several works have been reported in the literature on the application of microwave-irradiated transesterification process using homogeneous alkali catalyst [27, 28] and heterogeneous catalyst [29–31] for the production of biodiesel. Azcan et al. [28] have reported 93.7 and 92.2 % yield of bio-diesel for 1 wt.% KOH and 1 wt.% NaOH, respectively, within 1 min at 313 K under microwave heating. Encinar et al. [4] and Barnard et al. [22] have used continuous flow microwave methodology for the transesterification and reported this method to be more energy efficient than using a conventional heated apparatus. Apart from the great advantages of microwave-assisted reactions, there are few drawbacks with respect to scale up of the process. The most significant limitation in the scaling up of this technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimeters, depending on their dielectric properties. The safety aspect is another reason for rejecting microwave reactors in industry [32].

The analysis of the process parameters, specifically irradiation time and microwave output power, on the production of biodiesel from various sources under microwave irradiation have been reported in literature [3, 21–26], but the effect of holdup volume on the biodiesel production has not been reported in detail. The penetration depth of microwave radiation into the absorbing materials being an important parameter, the irradiation time and power are highly dependent on the volume of the material used in the production of biodiesel. The reaction parameters such as the volume of the batch and the vessel size play an important role in scale up.

The present work describes the microwave-assisted batch synthesis of biodiesel by varying the parameters like irradiation time and power, catalyst concentration, methanol to oil ratio for different batch volume of the reaction mixture. Catalyst amount, volume of the reaction mixture, irradiation time, and amount of methanol were considered as important parameters and optimized through central composite design to get maximum yield. Further the continuous biodiesel production studies were also performed using PTFE tubular reactor having two different holdup volumes (160 and 320 ml) to understand the volume effect, by varying parameters, namely, irradiation power, residence time, catalyst concentration, methanol to oil ratio. The parameters were optimized for maximum yield through Box–Behnken experimental design. Based on the batch and continuous process results the effectiveness of microwave irradiation for the biodiesel production was analyzed at different conditions based on the heat utilization through an effectiveness factor. The usefulness of the effectiveness factor determined for the batch and continuous processes has been discussed in detail.

2 Materials and methods

2.1 Materials

Karanja oil was purchased from a local departmental store. Analytical grade trioleins, methanol (99.8 %), KOH pellets, oxalic acid, isopropyl alcohol, and sodium sulfate were used without any further purification.

2.2 Experimental setup

2.2.1 Batch studies

All the batch experiments were conducted in a modified domestic microwave oven (Samsung M183DN), which has power output ranging from 100 to 800 W. A round bottom flask of 1,000 ml capacity with a Teflon agitator connected to a motor was used as the batch reactor. Carousel plate was replaced with a Teflon base in such a way that the carousel axis can rotate freely. A hole of 10 mm was made at the top of the oven to accommodate the condenser to aid in the reflux of methanol vapors. The experimental setup is as shown in Fig. 1.

Karanja oil with 0.8 % FFA was used for transesterification. Anhydrous potassium hydroxide (1.2 wt% based on oil weight) was dissolved in methanol (40 wt% based on oil weight) depending on the amount of oil so that the total reaction mixture would be 100 ml, 200 ml, 300 ml, 400 ml, and 500 ml respectively. The reaction mixture was mechanically agitated at 300 rpm for better dispersion of reactants and irradiated for different time intervals and irradiation power as per the experimental design. Immediately after the reaction, oxalic acid was added to neutralize the remaining potassium hydroxide. The product obtained was allowed to settle into two phases in a separating funnel. The mixture of products separated out as biodiesel (upper layer) and glycerol (lower layer). The biodiesel layer was further washed with equal volume of warm water three to four times and then dried over anhydrous sodium sulfate. The quality of biodiesel and triglyceride were analyzed through thermogravimetry method [25, 26, 33].

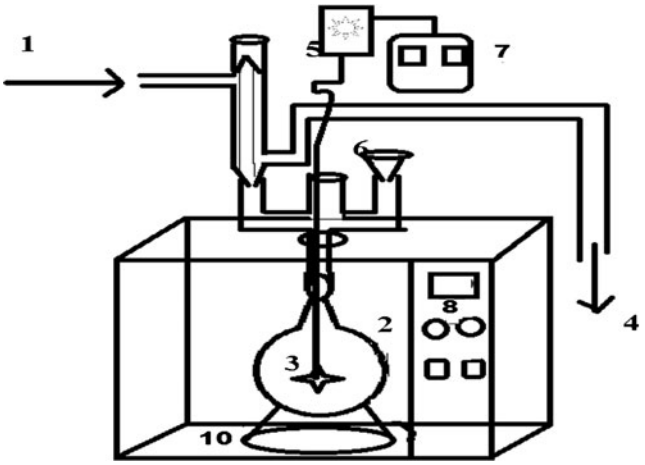

Fig. 1 Schematic diagram of domestic microwave oven modified for batch experiments. *1* water inlet, *2* microwave oven, *3* Teflon stirrer, *4* water outlet, *5* motor, *6* three neck adopter, *7* power supply, *8* operating buttons)

In order to optimize the transesterification reaction variables, response surface methodology [34] through the experimental design namely, central composite design (CCD) was applied. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. A five level–four factor central composite design consisting of 31 experiments (16 factorial points, eight axial points, and seven center points), was used to study the transesterification reaction variables [35, 36]. Catalyst amount, volume of the reaction mixture, irradiation time, and amount of methanol were chosen as independent variables in the experimental design for the response of percentage biodiesel yield. Transformation of variables from coded (X) to uncoded is as follows: $K=1.6+0.3X$; $V=300+100X$; $T=6+2X$; $M=40+5X$; where X can be −1, 0, or +1 (Table 1). The experimental data were fit to second-order polynomial equation to maximize percentage yield of FAME in transesterification step.

$$y = \beta o + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} x_i x_j \qquad (1)$$

Where 'y' is the response (%FAME Yield); 'x_i' and 'x_j' are uncoded independent variables and β_0, β_i, β_{ii}, and β_{ij} are intercept, linear, quadratic, and interaction constant coefficients, respectively. Minitab v15.0 software package was used for regression analysis and analysis of variance (ANOVA). Stepwise elimination of insignificant terms was carried out to obtain statistically significant reduced fit models. Optimal conditions obtained were validated by conducting experiments.

2.2.2 Continuous studies

Continuous experiments were conducted in a modified domestic microwave oven (Samsung TRIO) which can be operated with power output ranging from 100 to 850 W. The glass plate on the carousel was removed and a stationary ceramic tile cut to the size of the oven was fitted into the oven slightly above the carousel axis such that it can rotate freely. The surface on the top of the carousel axis was covered with aluminum foil to avoid randomly reflecting microwave radiation. A hole of 10 mm was made at the top of the oven. A poly-tetra-fluoro-ethylene (Teflon) tubular reactor (0.4 cm ID× 1,275 cm) of 160 ml volume was coiled into the oven and connected to the inlet pumps and the outlet reservoir at the back of the oven (as shown in Fig. 2). A larger tubular reactor having a volume of 320 ml (0.4 cm ID× 2,550 cm) was also used in this study.

Anhydrous potassium hydroxide was dissolved in methanol (based on oil weight) and the solution was transferred in to an oil-containing vessel. The vessel was equipped with an agitator, in which the reactants were agitated at 1,200 rpm by means of a mechanical agitator in order to prevent the phase separation. Then the reactants were continuously pumped in to the Teflon tubular reactor with different flow rates so that irradiation time could be varied. A three level–three factor Box–Behnken design [34] consisting of 15 experiments was applied to study the transesterification reaction variables. Catalyst amount, flow rate, and amount of methanol were chosen as independent variables in the experiment, the coded and un-coded levels of all variables are given in Table 2.

Table 1 Independent variables and levels used for experimental design in batch transesterification step

Variables	Levels				
	−2	−1	0	+1	2
KOH concentration, K (wt.%)	1	1.3	1.6	1.9	2.2
Volume of the reaction mixture, V (ml)	100	200	300	400	500
Irradiation time, T (s)	2	4	6	8	10
Methanol, M (wt.%)	30	35	40	45	50

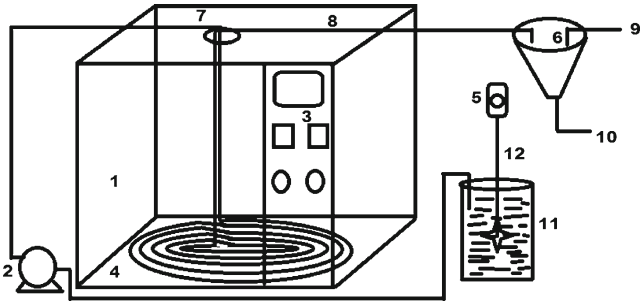

Fig. 2 Schematic diagram of domestic microwave oven modified for continuous experiments. *1* microwave oven, *2* pump, *3* operating buttons, *4* PTFE tubular reactor, *5* motor, *6* separator, *7* inlet, *8* outlet, *9* biodiesel outlet, *10* glycerol outlet, *11* tank, *12* agitator)

2.3 Energy efficiency of microwave irradiation process

In general, discussion about "energy efficiency" should always relate to comparable parameters. The question "whether microwave energy can be used more efficiently for the activation of chemical reactions?" cannot be answered spontaneously. Since the overall reaction may be the combination of chemical activation and microwave heating (volumetric heating), it is difficult to distinguish the effect of individual parameters on the conversion. In most of reports available in the literatures, the investigations were only carried out with very small amounts of reaction mixture in the millimole range, which were then irradiated with comparatively high power (300 to 1,000 W). Nüchter et al. [37] suggest that an "*effectiveness factor* (η)" that describes the efficiency of the microwave output power on the conversion would be a suitable approach to analyze how effective (in terms of heating) is the system. The effectiveness factor would be very less for investigation carried out at small scale, i.e., millimole scale. At small scale the amount of energy given to reacting molecules is very much larger than its capacity to consume. Considering a scale-up (mmol → mol → kmol), the importance of this approach becomes obvious. The fact that reaction parameters, such as the volume of the batch and the vessel size, play an important role in scale-up makes this approach a measure of efficiency of the system [32]. The determination of the energy input (Q_M) and the energy that is required to reach a certain temperature (Q_T) follows simple physical laws.

$$Q_M = P_M t \tag{2}$$

$$Q_T = m C_p \Delta T \tag{3}$$

$$\text{Effectiveness factor}(\eta) = Q_T / Q_M \tag{4}$$

The effectiveness factor is dimensionless and describes the effectiveness of the conversion of microwave energy into thermal energy. The available microwave output power P_M is determined by microwave device power settings. Therefore, the values calculated from Eq. 2 seem quite reliable [37]. In domestic microwave ovens, only the irradiation time and power can be varied as reaction parameters. Thus, the temperature is undetermined and increases steadily during irradiation. A possible but insufficient method to control the temperature is the on and off switching of the microwave field within a given time interval [38]. In modern laboratory microwave systems, which have computer controls, allow setting of the attainable temperature or pressure as limiting parameters. After reaching the required values of the preset parameters, the energy input is reduced to a level necessary for keeping the preset values [39]. In the present study, the bulk reactant temperature was measured immediately after the microwave oven switched off for the batch process and the continuous process it was measured at the product outlet. The effectiveness factors for the batch and continuous processes were measured at different conditions and compared with the percentage yield.

Table 2 Independent variables and levels used for experimental design in continuous transesterification step

Variables[a]	Levels		
	−1	0	+1
KOH concentration, *K* (wt.%)	1	1.2	1.4
Flow rate, *F* (ml/min)	25	50	75
Methanol, *M* (wt.%)	30	40	50

[a] Transformation of variables from coded (*X*) to uncoded is as follows: $C=1.6+0.2X$; $F=50+25X$; $M=40+10X$; where *X* can be −1, 0, or +1

3 Results and discussion

3.1 Batch studies

Initially the batch studies were performed to understand the effect of various parameters like irradiation time and power, and the reactant volume on biodiesel. The process parameters like methanol to oil ratio and KOH concentration were not considered in the present study, since these parameters have been extensively studied and reported in the literature [4, 25, 26].

3.1.1 Effect of irradiation time and power

In order to fix the power level for batch studies, reactant volume of 100 ml was used in the preliminary study by irradiating it under microwave for different irradiation times and powers (Fig. 3). From the results it was observed that the yield increased with increasing irradiation time for all

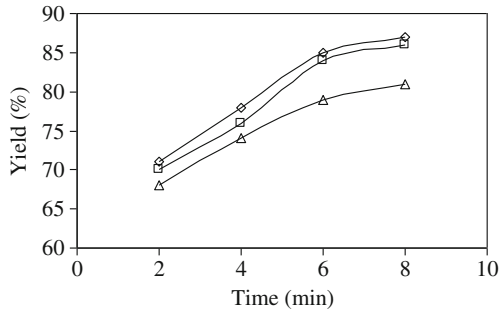

Fig. 3 Effect of irradiation time at different power level for 100 ml of the reaction mixture at a fixed methanol to oil ratio of 40 % *w/w*, KOH concentration 1.2 % *w/w*. *Square* 180 W, *diamond* 300 W, *triangle* 450 W

the power levels (180 to 450 W) and reached a more or less constant value at around 8 min of irradiation time. But the increase in the yield was not that much significant on comparison with the energy supplied to the system. When the power level was increased to 450 W, the yield was slightly decreased because of the fact that higher powers drastically increase the reaction temperature, which favors accelerated saponification of triglycerides [40]. Further the yield curve at 180 and 300 W were found approaching each other during all the irradiation time. Based on the above results, further experiments were conducted at a power level of 180 W.

3.1.2 Effect of volume and irradiation time

The effect of irradiation time on different volume of reactants were studied in batch mode on the yield of biodiesel at a fixed KOH concentration of 1.2 % *w/w*, methanol to oil ratio of 40 % *w/w*, and at an irradiation power of 180 W. The increase in the volume of reactant at a particular irradiation time and power (180 W) may reduce the biodiesel yield (Fig. 4). Since the microwave heating is a bulk heating process, the required reaction temperature cannot be reached in the whole volume of the reactants. This is due to the

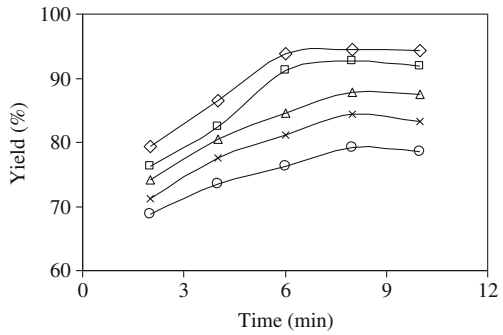

Fig. 4 Effect of irradiation time for different volumes of the reaction mixture at 180 W. Reactant volume: *diamond* 100 ml, *square* 200 ml, *triangle* 300 ml, *multiplication symbol* 400 ml, *circle* 500 ml

limitations in the penetration characteristics and intensity of the microwave, besides the physical properties of the contents of the reaction vessel. Further both the volume and geometry of the reaction vessel are crucial to provide uniform and reproducible heating. The microwave penetration does not depend only on the reacting molecules, but also depends on the material of reactor. Upon increasing the reactor volume, whole of the reaction mixture was not significantly influenced by the microwave irradiation. The input energy was insufficient for the reactants to attain the same reaction conditions as that at lower reactor volume. As a consequence the yield of biodiesel was reduced. On the other hand, as the irradiation time increased the reaction temperature increased to the required level by conjugated convection, which, in turn increased the yield of biodiesel to a maximum of 94.47 % at an irradiation time of 8 min (180 W). Moreover, the viscosity of reaction mixture decreased at higher irradiation time (higher temperature) and exposed the entire reaction mixture to the irradiation by increasing the conjugated convection. However, further increase of irradiation time beyond 8 min, did not improve the yield significantly.

3.2 Continuous studies

As mentioned in Section 2.2.2, a continuous flow tubular reactor was considered for the production of biodiesel. Based on the batch studies, the irradiation time, microwave power, and catalyst concentrations were fixed for the continuous reactor to study the effect of methanol to oil ratio. Since the dispersion of alcohol in oil is difficult in the continuous process configuration (tubular), the authors perceived that the higher methanol to oil ratio may be required to obtain high yields.

3.2.1 Effect of methanol to oil ratio

The effect of methanol to oil ratio on the yield of biodiesel was studied at a fixed KOH concentration of 1.2 % *w/w* in a PTFE tubular reactor having a holdup of 160 ml, at an irradiation power of 100 W (Fig. 5) and 180 W (Fig. 6), respectively. Analysis of both the Figs. 5 and 6 indicated that, at lower methanol to oil ratio the yield was less due to lower quantity of alcohol available. In general, the transesterification reaction is a reversible reaction and excess alcohol is required in order to drive the reaction in the forward direction (product side). Hence an increase in the methanol to oil ratio increased the yield and it reached a maximum of 91.82 % at an irradiation time of 8 min, power of 180 W and methanol to oil ratio of 40 % *w/w* (11:1 molar ratio). Increasing methanol to oil ratio beyond 40 % did not improve the yield [4, 25]. As the residence time increased the yield also increased, due to the lower flow rate and

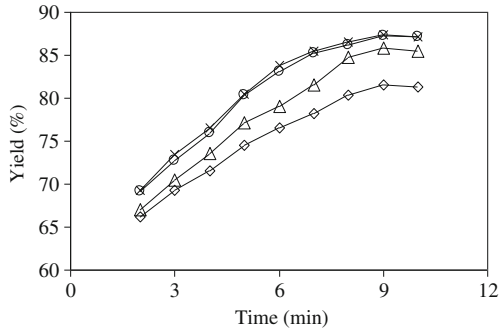

Fig. 5 Effect of methanol to oil ratio at an irradiation power of 100 W. Methanol to oil ratio (*w*/*w*): *diamond* 30 %, *triangle* 35 %, *multiplication symbol* 40 %, *circle* 50 %

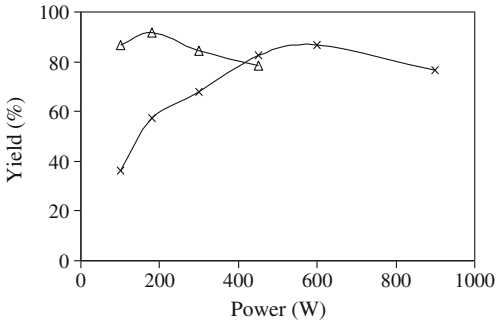

Fig. 7 Effect of power on yield at a fixed catalyst concentration of 1.2 % *w*/*w* and 40 % *w*/*w* methanol. *Triangle* 160 ml holdup at 8 min residence time, *multiplication symbol* 320 ml holdup at 9 min residence time

longer exposure time for the reactants. At lower residence time (higher flow rate) the reaction mixture was not exposed to the microwave irradiation for sufficient time in order to get the required dielectric heating and achieve higher yield. The mixture was well irradiated at the decreased flow rate (or the increased residence time), thus increasing the yield and a maximum yield was obtained at the residence time of 9 min for 100 W (Fig. 5) and 8 min for 180 W (Fig. 6). Increasing the residence time beyond this point did not improve the yield significantly due to higher temperature (beyond methanol boiling point).

3.2.2 Effect of MW irradiation power on yield

In order to know the effect of irradiation power on the yield, experiments were conducted holding the process parameters at values where the highest yield was observed in the continuous process for two different tubular dimensions with a holdup volume of 160 and 320 ml. The reaction mixture was irradiated at 100, 180, 300, and 450 W with an 8-min residence time for the smaller tubular reactor (holdup volume of 160 ml) and up to 900 W and 9-min residence time for the bigger reactor (holdup volume of 320 ml; Fig. 7). It was found that the increase in irradiation power had negative effect beyond 180 W for the holdup of 160 ml and 600 W for the holdup of 320 ml on the yield due to the drastic increase in reaction temperature, which favored the saponification of triglycerides [41] and generation of methanol vapor. At higher power, the methanol vapor generated reduced the availability of the methanol for the reaction. The lower yield was obtained in the 320 ml holdup configuration till 300 W (Fig. 7) due to the lower intensity of the MW irradiation, which may not be sufficient to heat up the reaction contents to the desired temperatures.

3.2.3 Effect of irradiation time on yield

In order to know the effect of irradiation time at different irradiation power on the yield of biodiesel, experiments were conducted in a PTFE tubular reactor having 320-ml holdup with various residence times. From Fig. 8, it can be observed that the yield increased with increasing residence time. Since the flow rate was high at the lower residence time, the reaction mixture was not exposed to the microwave irradiation for sufficient time to get the required dielectric heating [4]. In contrast, the reactants exposed to irradiation for longer time at lower flow rate produced better

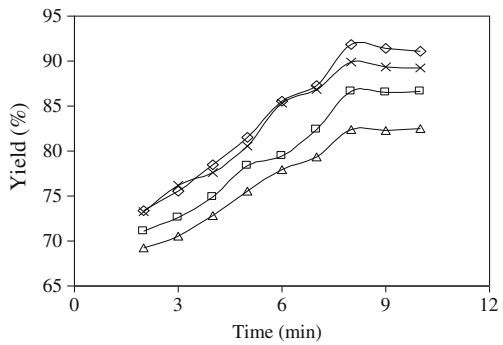

Fig. 6 Effect of methanol to oil ratio at an irradiation power of 180 W. Methanol to oil ratio (*w*/*w*): *triangle* 30 %, *square* 35 %, *diamond* 40 %, *multiplication symbol* 50 %

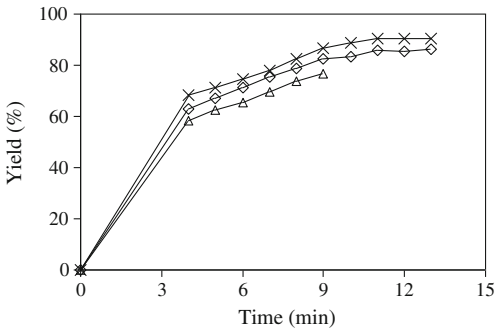

Fig. 8 Effect of irradiation time at a fixed catalyst concentration of 1.2 % *w*/*w* and methanol to oil ratio of 40 % (*w*/*w*) with different irradiation power. *Diamond* 450 W, *multiplication symbol* 600 W, *triangle* 900 W)

Table 3 Central composite experimental design points and response as the yield of biodiesel obtained through batch transesterification

Std. order	Levels of variable uncoded (coded)				Yield	
	C	*M*	*V*	*T*	Exp.	Predicted
1	1.3 (−1)	35 (−1)	200 (−1)	4 (−1)	77.46	76.02
2	1.9 (1)	35 (−1)	200 (−1)	4 (−1)	62.47	62.65
3	1.3 (−1)	45 (1)	200 (−1)	4 (−1)	82.53	82.52
4	1.9 (1)	45 (1)	200 (−1)	4 (−1)	69.16	67.82
5	1.3 (−1)	35 (−1)	400 (1)	4 (−1)	71.32	70.54
6	1.9 (1)	35 (−1)	400 (1)	4 (−1)	57.49	56.48
7	1.3 (−1)	45 (1)	400 (1)	4 (−1)	78.12	77.28
8	1.9 (1)	45 (1)	400 (1)	4 (−1)	62.54	61.86
9	1.3 (−1)	35 (−1)	200 (−1)	8 (1)	85.27	85.40
10	1.9 (1)	35 (−1)	200 (−1)	8 (1)	72.66	71.26
11	1.3 (−1)	45 (1)	200 (−1)	8 (1)	91.47	90.24
12	1.9 (1)	45 (1)	200 (−1)	8 (1)	74.52	74.75
13	1.3 (−1)	35 (−1)	400 (1)	8 (1)	79.54	78.64
14	1.9 (1)	35 (−1)	400 (1)	8 (1)	64.35	63.80
15	1.3 (−1)	45 (1)	400 (1)	8 (1)	84.47	83.75
16	1.9 (1)	45 (1)	400 (1)	8 (1)	68.32	67.54
17	1.0 (−2)	40 (0)	300 (0)	6 (0)	87.57	89.07
18	2.2 (2)	40 (0)	300 (0)	6 (0)	58.24	59.52
19	1.6 (0)	30 (−2)	300 (0)	6 (0)	66.45	67.91
20	1.6 (0)	50 (2)	300 (0)	6 (0)	78.86	78.16
21	1.6 (0)	40 (0)	100 (−2)	6 (0)	81.27	82.34
22	1.6 (0)	40 (0)	500 (2)	6 (0)	67.86	69.60
23	1.6 (0)	40 (0)	300 (0)	2 (−2)	60.27	61.82
24	1.6 (0)	40 (0)	300 (0)	10 (2)	75.63	76.86
25	1.6 (0)	40 (0)	300 (0)	6 (0)	71.43	71.36
26	1.6 (0)	40 (0)	300 (0)	6 (0)	70.52	71.36
27	1.6 (0)	40 (0)	300 (0)	6 (0)	72.67	71.36
28	1.6 (0)	40 (0)	300 (0)	6 (0)	71.89	71.36
29	1.6 (0)	40 (0)	300 (0)	6 (0)	70.82	71.36
30	1.6 (0)	40 (0)	300 (0)	6 (0)	72.43	71.36
31	1.6 (0)	40 (0)	300 (0)	6 (0)	70.80	71.36

yield. The maximum yield of more than 91 % was obtained at a residence time of 11 min with 600 W irradiation power. A large amount of methanol vaporization was observed, and hence experiments were not conducted beyond 9 min for an irradiation power of 900 W.

3.3 Optimization of process parameters

3.3.1 Batch process

The complete CCD matrices together with the experimental and predicted values obtained for biodiesel yield as response at the design points for batch experimentation are given in Table 3. All the variables are shown in both coded and uncoded (actual) form. The experimental data were fitted to a quadratic polynomial equation through least square technique and statistical analyses were carried out for the same. Upon stepwise elimination of insignificant terms, the significant terms were fitted to a reduced model.

Regression coefficients of predicted quadratic polynomial after stepwise elimination shows (Table 4) that linear and quadratic term of *K*, *M*, *V*, and *T* are significant model terms for optimizing the yield. However, the interaction terms have no effect on yield of biodiesel. High coefficient of determination 0.981 shows that model is highly significant. The predicted quadratic polynomial equation may be represented by Eq. 5 as follows;

$$\%\text{FAME Yield} = 167.712 - 58.367K - 0.114V + 1.878T - 1.529M + 10.54K^2 + 0.00014V^2 + 0.025M^2 \quad (5)$$

The contour plots were further plotted to study the interaction effect of process parameters on the biodiesel yield in

Table 4 ANOVA for the batch process model equation (Eq. 5)

Term	Regression Coef.[a]	SE Coef	*T* value	*P* value
Constant	167.712	18.1246	9.253	0.0001
K	−58.367	8.7794	−6.648	0.0001
V	−0.114	0.0150	−7.582	0.0001
T	1.878	0.1348	13.932	0.0001
M	−1.529	0.7878	−1.941	0.065
*K***K*	10.540	2.7291	3.862	0.001
*V***V*	0.000136	0.0001	5.552	0.0001
*M***M*	0.025	0.0098	2.590	0.016
Lack-of-fit	R^2=98.1 %		*F* value=11.65	*P*=0.003

[a]Significant at 95% confidence level

batch process using the Eq. 5. The 0 level values for each variable were kept as constant to draw the contours between the other variables. Figure 9 shows the contour plots for the batch process. In Fig. 9a–c, as the catalyst concentration increased the yield decreased with decrease in methanol ratio (Fig. 9a), with increase in volume of the reaction mixture (Fig. 9b) and with decrease in irradiation time (Fig. 9c). This is due to the fact that higher catalyst concentration leads to more soap formation. From the Fig. 9a, d, and e, it was observed that the lower methanol ratios gave lesser yield with increase in volume (Fig. 9d) and with decrease in irradiation time (Fig. 9e). This could be ascribed to the equilibrium nature of the reaction. Low irradiation times are not sufficient to provide the necessary dielectric heating for higher volume and lower methanol ratio, which is evident from Fig. 9e and f, respectively. Further, when the irradiation time was increased for the higher volume of reactant, convectional currents generated in the reaction mixture made the system to become homogeneous in terms of heat transfer. Hence the biodiesel yield improved for larger volumes at higher irradiation times.

The optimized values of independent variables were found to be as follows: catalyst concentration (*K*) of 1.13 % *w*/*w*,

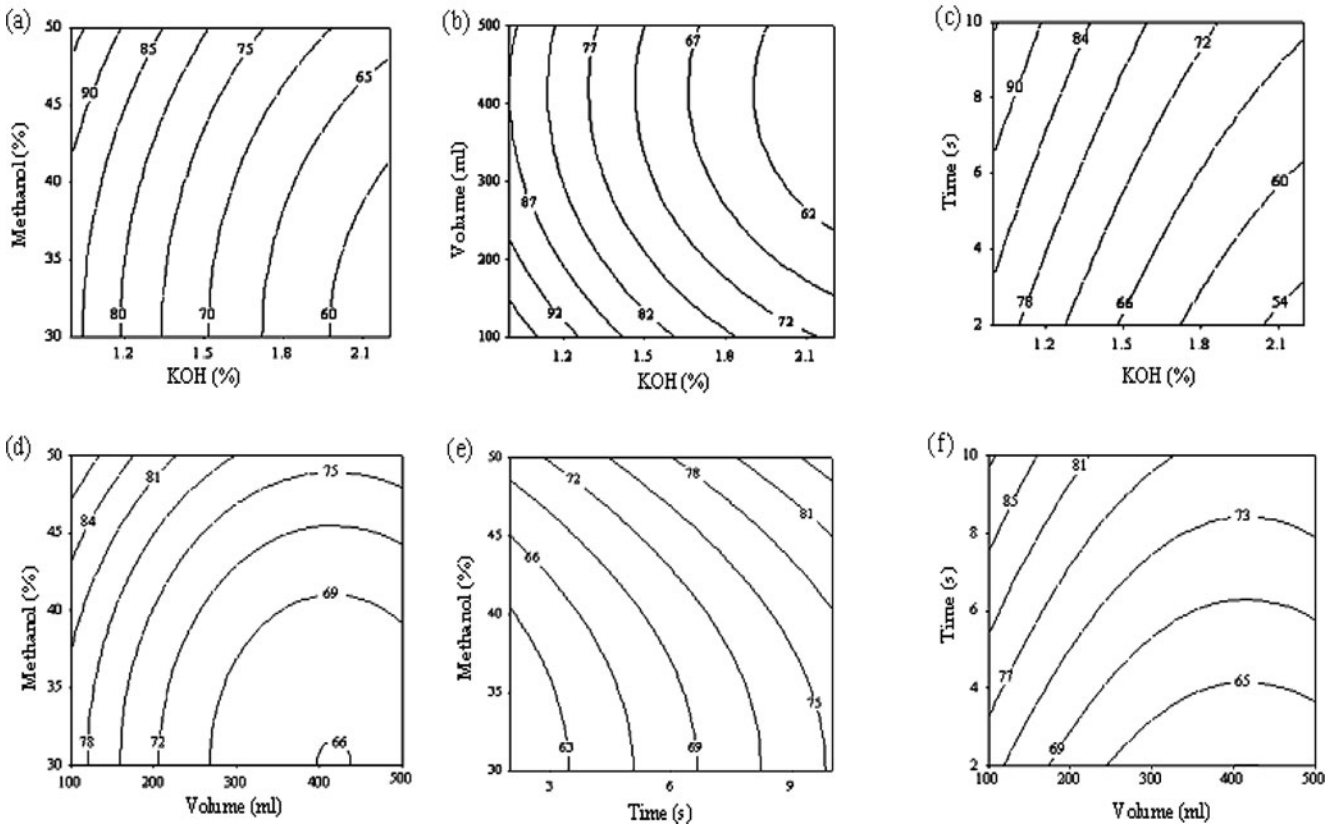

Fig. 9 Contour plots of yield predicted from the batch process variables through quadratic model equation (Eq. 5)

Table 5 Box–Behnken experimental design and response for continuous process

Std. order	Levels of variable un coded (coded)			Yield (%)	
	C	*F*	*M*	Exp	Predicted
1	1.0 (−1)	25 (−1)	40 (0)	83.57	82.6
2	1.4 (1)	25 (−1)	40 (0)	79.48	79.12
3	1.0 (−1)	75 (1)	40 (0)	72.28	72.63
4	1.4 (1)	75 (1)	40 (0)	65.38	66.35
5	1.0 (−1)	50 (0)	30 (−1)	68.49	68.85
6	1.4 (1)	50 (0)	30 (−1)	64.12	63.87
7	1.0 (−1)	50 (0)	50 (1)	74.57	74.82
8	1.4 (1)	50 (0)	50 (1)	70.41	70.04
9	1.2 (0)	25 (−1)	30 (−1)	78.42	79.02
10	1.2 (0)	75 (1)	30 (−1)	69.54	68.82
11	1.2 (0)	25 (−1)	50 (1)	85.54	86.26
12	1.2 (0)	75 (1)	50 (1)	74.32	73.72
13	1.2 (0)	50 (0)	40 (0)	77.27	77.12
14	1.2 (0)	50 (0)	40 (0)	76.54	77.12
15	1.2 (0)	50 (0)	40 (0)	77.56	77.12

methanol to oil ratio (*M*) of 36.72 % *w/w*, 100 ml of the reaction mixture (*V*) and a residence time (*T*) of 6.4 min. Few experiments were conducted at optimal condition to validate the model. The final yield value at this condition was determined to be 90.14±0.57 %. This value is reasonably close to the predicted yield of 90.14 %.

3.3.2 Continuous process

The Box–Behnken method was applied to design the experimental points for the optimization of the continuous process through response surface methodology. The complete design matrices together with the experimental and predicted values of biodiesel yield as response at the design points for continuous experimentation is given in Table 5. The experimental data were fitted to quadratic polynomial equation through least square technique and statistical analyses. Upon stepwise elimination of insignificant terms (Table 6), the significant terms were fitted to reduced model and were found to be:

$$\%\text{FAME Yield} = -116.423 + 272.9\,K - 0.676\,\text{F} + 2.683\,M - 118.79\,K^2 + 0.004\,F^2 - 0.03\,M^2 \quad (6)$$

At a fixed methanol to oil ratio (Fig. 10g) yield increased as the flow rate decreased as the reaction mixture was not well irradiated at lower residence times. Further, if the catalyst concentration was increased beyond 1.2 % *w/w*, the increase in yield was not significant due to soap formation. At a fixed flow rate (Fig. 10h), increasing the methanol to oil ratio with lower concentrations of catalyst did not lead to higher yield. As the catalyst concentration was increased in the range of 1.1–1.3 % *w/w*, the required amount of methanol to oil ratio decreased for higher yield. In addition, increment in catalyst concentration with both higher and lower methanol to oil ratio decreased the yield. At a fixed catalyst concentration (Fig. 10i) as the flow rate decreased the yield increased at higher methanol to oil ratios. The variables were optimized through response surface methodology and the optimized values of

Table 6 ANOVA for the continuous process model (Eq. 6)

Term	Regression Coef[a]	SE Coef	*T* value	*P* value
Constant	−116.423	21.3661	−5.449	0.001
K	272.900	31.6413	8.625	0.00001
F	−0.676	0.0854	−7.916	0.00001
M	2.683	0.4227	6.346	0.00001
*K***K*	−118.792	13.1628	−9.025	0.0001
*F***F*	0.004	0.0008	5.329	0.001
*M***M*	−0.030	0.0053	−5.649	0.00001
Lack-of-fit	R^2=98.5%		*F* value=4.61	*P*=0.18

[a]Significant at 95 % confidence level

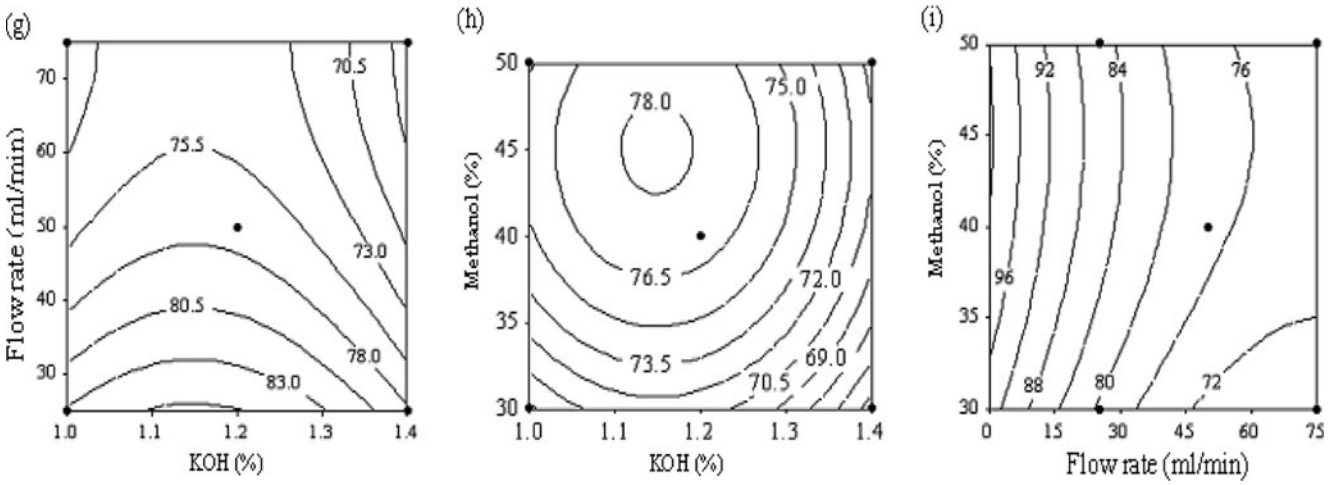

Fig. 10 Contour plots of yield predicted from the continuous process variables through quadratic model equation (Eq. 6)

independent variables were found to be as follows: KOH concentration (K) 1.22 (w/w) %, methanol–oil ratio (M) 49.5 and a flow rate (F) of 25.21 ml/min. Few experiments were conducted at optimal condition to validate the model. The final yield at this condition was determined to be 84.97± 1.46 %.

3.4 Effectiveness of the microwave irradiation

The effectiveness factor (Eq. 4) for present method of synthesis was calculated and plotted in Figs. 11 and 12. The power input calculated here is not a simple product of power and total time. Instead, in the domestic microwave oven the magnetron delivered constant power of 850 W per minute and this takes place for few seconds and then no power is delivered for next few seconds, i.e., controlled on/off cycle according to the power rating of the equipment. The rate of this on/off cycle was considered for calculation of P_M. As an example, for 100 W power magnetron ejects 850 W/min for 3.5 s in two cycles in a minute, i.e., for 3.5 s the magnetron delivers the power and then no power is delivered for next 26.5 s. This cycle is repeated for every 30 s. Hence if the reaction is carried out for 2 min, then power input would be 850 W×2 min×7 s/min=13,600 J. The mass of biodiesel produced varies with different power level and also with the irradiation time. Hence to avoid ambiguity in results, energy was calculated on the basis of kilograms of reactant used for the process. To calculate Q_M the specific heat of oil and methanol were considered. The specific heat of methanol is 2.7 J/g °C and of oil is 1.9 J/g °C. Based on this at the given molar ratio the averaged specific heat was considered for the calculation of Q_M. The specific heat calculated according to this method may not be the actual value, since the composition of reaction mixture is dynamic with irradiation time. During the reaction, the product molecules like fatty acid esters and glycerol are generated and their concentration depends on the reaction time. Hence the determination of actual specific heat of the mixture may be possible only if the product formation rate is available. In the present study, the effectiveness factor was calculated only based on the inlet reactants and their composition. The temperature difference between the output temperature of the reaction mixture and room temperature was considered for the calculation.

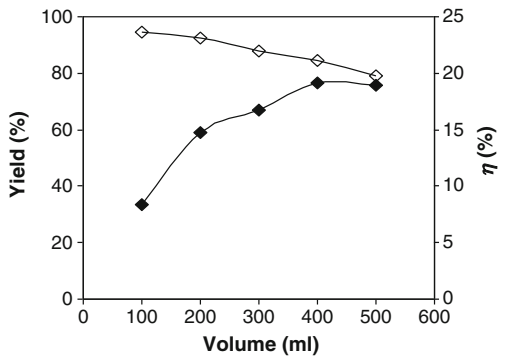

Fig. 11 Effect of batch reactant volume on effectiveness factor. *White diamond* yield (%); *black diamond* η (%)

To understand the effect of reactor volume on effectiveness factor at a constant power, experiments were conducted at 180 W for different reactant volume in batch mode. The effectiveness factor and percentage yield at different batch volumes were plotted (Fig. 11). From the Fig. 11, it was observed that the effectiveness factor increases with increasing batch volume, but the yield was found to decrease with volume. At higher volume, the amount of microwave energy absorbed by the reactant is comparatively high, however the reactant mixture may not attain the required reaction temperature for the specific irradiation time (8 min), resulting in the reduction of yield. The effectiveness factor was very less

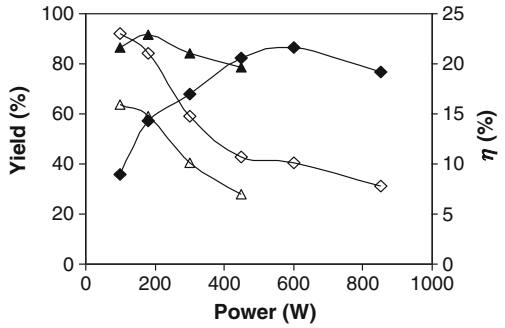

Fig. 12 Effect of power on effectiveness factor for the continuous tubular configuration. Holdup volume of 160 ml: *black diamond* yield (%); *white diamond* η (%), holdup volume of 320ml; *black triangle* yield (%); *white triangle* η (%)

in 100 ml batch (8.3) but the yield was high (94.87 %) when compared to all the other batch volumes. But this is obvious for the reason that a small amount of reactants are irradiated at high power for long enough time. In case of larger batch (500 ml) the effectiveness factor increased significantly and reached a value of 19 with a reduction in yield (79 %). The experimental findings suggested that the insufficient temperature for the reaction at higher volume may be due to the limited penetration of the microwave in the reactant material and insufficient exposure of the material to microwave. Further, to improve the yield, the reactant may be irradiated for longer time with appropriate reactor configuration. Simple batch type equipment may not be sufficient to overcome the restrictions offered by the microwave irradiation.

The experiments were further conducted in a tubular configuration having two different holdup volumes of 160 and 320 ml to enhance the effectiveness factor of the microwave irradiation process. In 160 ml holdup configuration, the Teflon tube was coiled in a single layer at the bottom of the microwave oven cavity and the reactants were irradiated for different power levels (100, 180, 300, and 450 W) at a residence time of 8 min. For 320-ml holdup configuration the length of the tube required was double when compared to the 160 ml holdup process and the tubes were coiled in two layers with sufficient distance. Experiments were conducted in this configuration at different power levels (100 to 850 W) with a residence time of 8 min. The effectiveness factor and percentage yield for all the experiments with both 160 and 320 ml holdup configurations were plotted (Fig. 12). From the Fig. 12, a trend very similar to batch process is observed. Here the effectiveness factor increased and the percentage yield decreased with increasing reactor holdup volume. Further the effectiveness factor was found to decrease for both the holdup volumes with power due to the inefficiency of microwave absorption at higher powers. However, the percentage yield increased up to certain power level (180 W for 160 ml holdup and 600 W for 320 ml holdup) then started to decrease beyond this power level. The results for the continuous tubular reactor also suggest a trend similar to batch process. However, the effectiveness factor increased in the tubular configuration, as compared with the batch process, for the equal volume of holdup and residence time at 180 W (holdup volume 160 ml, η=11.8 for batch process and η=14.8 for tubular process; holdup volume 320 ml, η=17.8 for batch process and η=21 for tubular process; Figs. 11 and 12) due to the higher exposure of the reactant to microwave irradiation. From the analysis of Figs. 11 and 12, it can be concluded that the effectiveness factor may be increased by increasing the reactor holdup volume with enhanced microwave irradiation exposure area. A reactor configuration with area larger surface area to volume ratio for MW exposure may decrease the thickness of the material, which overcomes the penetration limitation of the microwave irradiation processes. Further to enhance the MW absorption, wave guides, which can guide the MW directly to the materials surface, may also be considered for the future development of reactor configurations.

3.5 Properties of biodiesel

The biodiesel synthesized through microwave-assisted batch/continuous transesterification process were analyzed for some of the important physical and chemical properties. The result are summarized and compared with the ASTM D6751-09 [41] standards (Table 7). The density, viscosity, acid value, and FFA were found to be within the limits of ASTM standard, which confirms the suitability of the microwave-assisted production of biodiesel as engine fuel. The cetane index has not changed much when compared to the feed oil, as a result of unchanged iodine value and saponification number. The FAME content or ester content is also within the limits of ASTM standards, which confirms the purity of the biodiesel.

Table 7 Properties of Karanja biodiesel synthesized through microwave-assisted transesterification

Properties	Karanja biodiesel	ASTM D6751-09
Density (kg/m^3)	885	860–900
Kinematic viscosity (mm^2/s)	4.3	1.9–6.0
Acid value (mg KOH/g)	0.42	<0.5
Saponification no. (mg KOH/g)	227	–
Iodine value (g I_2/100 g)	82.6	–
Cetane index	56.5	>47
Ester content	97–99	>96.4

4 Conclusions

Karanja biodiesel was successfully synthesized in a microwave-assisted batch/continuous process. Effects of volume of the reaction mixture, irradiation time, and irradiation power on the yield of biodiesel have been discussed. Using standard RSM design with the elimination of the insignificant model terms, a quadratic polynomial equation was developed to predict the yield of biodiesel in a batch reactor. The results obtained in the optimization are as follows: catalyst concentration of 1.13 % *w*/*w*, methanol to oil ratio of 36.72 % *w*/*w*, 100 ml of the reaction mixture, and a residence time of 6.4 min. Two different continuous reactors having the holdup of 160 and 320 ml were also used for the biodiesel production. Optimization of process parameters of continuous reactor was carried out by using Box–Behnken experimental design. Optimal parameters were found to be as follows: KOH concentration (K) 1.22 (*w*/*w*)%, methanol–oil ratio (M) 39.49 (*w*/*w*)% and a flow rate of 25.21 ml/min. An optimum yield of more than 90 % was achieved at a residence time of 11 min.

The effectiveness factor analysis revealed that approximately 20 % MW energy supplied was only utilized for the continuous process which is higher than the batch effectiveness value. Further it was found that the effectiveness factor increased with increasing batch volume and MW exposure surface area and decreased with increasing power. The experiments and the results of the microwave-irradiated process, in particular, the variable volume and effectiveness factor, are very much useful for the scale-up of biodiesel production to the industrial scale.

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